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Risø National Laboratory, Roskilde, Denmark,

PULSED PLASMA DEPOSITED MALEIC ANHYDRIDE THIN FILMS AS FUNCTIONALISED SURFACES IN COMPOSITE MATERIALS

Joanna Drews[a], Stergios Goutianos[d], Keld West[c], Søren Hvilsted[b], Kristoffer Almdal[a]

[a] Polymer Department, Risø National Laboratory, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde
[b] Danish Polymer Centre, Technical University of Denmark, Produktionstorvet 423, DK-2800 Kgs. Lyngby
[c] Nano-Science Center, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen
[d] Materials Research Department, Risø National Laboratory, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde

ABSTRACT

A low power AC 2-phase plasma setup was used for surface deposition of thin films of maleic anhydride (ppMAH) on glassy carbon or on polyethylene. The planar glassy carbon substrate models carbon fibres in composite materials. The substrates are treated with different plasma power levels. The present study focuses on the effect of plasma power on the surface chemistry, the properties of the modified layers and the adhesion between the substrates and an epoxy resin (interface properties). The discussion of the surface characteristics is based on surface chemistry analyses (XPS and toluidine blue staining method) and the interfacial fracture energy (measured by the double cantilever beam test method). To explain the observed differences in interfacial fracture energy, some of the samples were hydrolysed in alkaline solution. The hydrolysis ratio of preserved anhydride groups on the surface was monitored with the toluidine blue staining method.

1. INTRODUCTION

It is well known that the macroscopic properties of composite materials are strongly dependent on the integrity of the fibre-matrix interface. The optimisation of the fibre-matrix interface is essential for improved physical and in particular mechanical properties of fibre reinforced polymer composites. The adhesion between the fibres and the matrix is realised through bonds

which play an essential role for the interface strength, especially in the case of polymeric materials, which often consist of cross-linked constituents (Hansen (1999), Doi (1996), Launay et al, (2007)). The cross-links can be either covalent bonds or physical interactions, e.g. hydrogen bonds or dispersion and electrostatic forces. The Hansen solubility parameters can help in quantifying the physical affinities between the constituents.

Wet/solution chemistry is usually used to surface modify the fibres, whereas plasma treatment is mostly being used for cleaning (Keller et al (2005)). In this study the authors used the plasma polymerisation technique as a method of fibre surface modification by thin polymeric film deposition. The advantage of plasma polymerisation is that it is a solvent-free technique, which is rather easy and inexpensive to use. Post-treatment e.g. cleaning and purifying of the samples is not necessary unless further modifications are desired. The structure of plasma polymerised layers is usually very complex and thus difficult to understand and analyse. Properly understood and controlled, the complex structure can, however, be used in designing new high strength composite materials by tailoring the fibre/matrix interface or interphase.

The complex nature of layers modified with pulsed plasma comes from two processes taking place simultaneously, one is the polymerisation (time *off* – time for inactive plasma where addition of monomer molecules progress) and the other is creating radicals (mostly on the surface; time *on* – time for active plasma). The time *on* and *off* influences the chemistry and properties of polymerised layers (Schiller et al (2002)). Using the SoftPlasma™ technique the ratio between times *on* and *off* were controlled by the plasma power level – a higher plasma power level thus results in a more active (more radicals) polymerisation. The output of this process could be observed as an increase of the polymerisation rate (with constant flow of monomer and Ar). The plasma polymers created with low power are expected to have a high content of low molecular weight polymers. This could mean that the modified layer actually contained oligomers instead of polymers and was only weakly cross-linked. This material could often be easily dissolved. Hence, to obtain a stable layer of polymer, it is necessary that the power input to the system exceeds a minimum energy (Hegemann et al (2005)).

For the surface modification in the present study we used maleic anhydride (MAH). The layers of pulsed (rf) and continues (CW) plasma polymerised maleic anhydride (ppMAH) had previously been investigated and characterised using surface characterisation techniques (Ryan et al (1996)). It was concluded from their work that with manipulation of plasma power it is possible to preserve anhydride groups during the plasma polymerisation. The system of SoftPlasma™ used power less than 1 W/l. The distinct advantage of this plasma polymerisation method is that the required energy supplied into the system is low enough to run the polymerisation in a way very close to the conventional way (polymerisation in the solution).

In this paper we focus on the characterisation of the surface coatings made by soft plasma polymerisation of maleic anhydride. We also showed that the complex nature of the polymeric coating can be advantageous. The surface chemistry is analysed with X-ray photoelectron spectroscopy (XPS) and the toluidine blue staining method (Sano et al (1996)). The rate of hydrolysis of preserved anhydride groups, in the ppMAH films, during plasma surface modification as a function of plasma power levels was investigated. The hydrolysis ratio was monitored by touidine blue staining. The fracture energy of the planar glassy carbon/epoxy interface was measured under nominal Mode I using the double cantilever beam method test method.

2. EXPERIMENTAL SECTION

Materials. Planar glassy carbon substrates (SIGRADUR G) were purchased from HTW Hochtemperatur, Germany in sizes of 20x20x1 mm^3 and 65x5x1 mm^3. Polyethylene (PE) foil (thickness 1 mm) was extruded in-house from BOREALIS FA 3220 granules. Toluidine Blue O was obtained from Sigma Aldrich and stored at room temperature in the dark. Maleic anhydride (MAH) was obtained from Sigma Aldrich as briquettes, which were ground into fine powder in a hood and placed in a metal container under vacuum. Ultra-pure water was obtained using a MilliQ system from Millipore.

Substrate preparation. The PE substrates were cleaned in an ultrasonic bath for 5 minutes in different solvents, including acetone, methanol and miliQ water. The glassy carbon substrates were cleaned in an ultrasonic bath in different solvents, using chloroform (5 minutes), acetone (twice – 2x5 minutes) and methanol (5 minutes). Finally, all substrates were dried with a jet of argon. The cleaned substrates were stored in polystyrene Petri dishes until use. The substrates were stored no longer than a few hours before the surface modification, after which they were kept under vacuum in the plasma chamber until further use.

Plasma polymerisation. The plasma chamber set-up is described in detail by Winther-Jensen et al. (2003; 2004) and Ademovic at al. (2005). This plasma coating technique, called SoftPlasma™. The process of plasma polymerisation is described in detail by Drews et al. (2007). The plasma polymerisation information is given in units of power per litre (W/L) and plasma polymerisation time (min). The power of the plasma may be calculated from the formula $P = \frac{U * I}{Vol}$, where U is the voltage across the chamber, I is the current during plasma polymerisation, and Vol is the plasma volume equal to 11.5 l. In order to obtain a uniform coating on both sides, the PE substrates were suspended freely close to the centre of the plasma chamber and a 10 mm wide border around the edges was discarded. The glassy carbons for the mechanical tests were mounted on double sticky tape on a glass tube.

Surface analysis. X-ray photoelectron spectroscopy (XPS) was performed using a SPECS Sage 100 instrument with a non-monochromatic MgK_α X-ray source at a power of 275 Watts (11 keV and 25 mA). The pressure in the chamber was always below 1 x 10^{-7} mbar. Two kinds of spectra were obtained: survey and high resolution. Atomic concentration of the surface composition was calculated from the intensity of the peaks of survey spectra (0-1100 eV, 100 eV pass energy). The high resolution spectra (23 eV pass energy) of surface components was used to fit 4 peaks with full-width at half-maximum (FWHM) of 2.0 eV. The positions of the peaks was as follow: 285.0 eV for C-C/C-H (referencing peak), 286.5 eV for C-O, 288.0 eV for C=O, 289.4 eV for C(O)O.

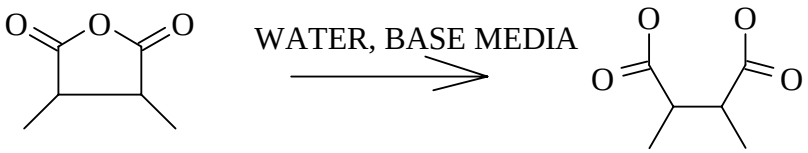
Fracture mechanics test. Double Cantilever Beam (DCB) sandwich specimens were prepared using the plasma treated glassy carbon wafers (65x5x1 mm^3). The resin used was an epoxy system (Prime-20, SP Systems, UK). The resin and the hardener were mixed at a weight ratio of 4:1, degassed for 2x5 min under full vacuum, and then casted into silicon rubber moulds between two glassy carbon wafers. Teflon films (0.5 mm in thickness) were used to keep the wafers apart and to create a notch of 20 mm in length necessary to initiate a crack along the glassy carbon-epoxy interface. The DCB specimens were cured for 24 hours at room temperature and subsequently post-cured at 50°C for 16 hours. The cured samples were ground and polished to facilitate optical observations of the interface crack growth. Subsequently, the sandwich specimens were glued on specially made stainless steel beams (6 mm in thickness) that could be mounted on the test fixture. An epoxy adhesive (Scotch Weld) was used to glue

the DCB specimens to the steel beams. The curing time for the adhesive was 24 hours at room temperature. More detailed description of the DCB method can be found in the following references: Bao et al (1992) and Sørensen et al. (1996)

Surface derivatisation. The toluidine blue surface derivatisation method of Sano et al (1993) was used to determine the number of carboxylic acid groups in the volume of the coatings. In brief, a polyethylene plate with size 20x20x1 mm^3 modified on both sides (the reactive area of the surface is approximately 8 cm^2) was incubated with 5 ml of fresh toluidine blue solution ($2x10^{-4}$ M) in 0.1 mM NaOH for 1 hour at 40^{o}C in a water bath. Each carboxylic acid group was assumed to bind one molecule of toluidine blue. Afterwards, the solution was removed and the surface rinsed 3 times with fresh 0.1 mM NaOH. The samples were placed in clean, dry HDPE flasks with 5 ml of 50% (v/v) acetic acid for 30 minutes at 40^{o}C to release the bound toluidine blue into the solution. The absorbance of the solutions was measured with a UV-1700 Shimadzu spectrophotometer at a wavelength of 630 nm. The number of reactive carboxylic acid groups in the films was determined from a standard curve of toluidine blue.

3. RESULTS AND DISCUSSION

Surfaces were modified with pulsed plasma maleic anhydride (ppMAH) with different power levels (0.3, 0.7, 1.2 W/l) in such a way that the thickness of the films remained the same (approx. 80 nm). The freshly deposited layer of ppMAH on PE was placed into 0.1 mM NaOH for hydrolysis of the preserved anhydride groups on the surface. After hydrolysis of an anhydride group two carboxylic acid groups are obtained:



From XPS analysis we had previously shown that the surface chemistry was not influenced by plasma power level (Drews et al. (2007)). The XPS technique is a surface sensitive method, where about 70% of the signal comes from the first monolayer (approx. 1 nm). Only the last 30% comes from deeper layers (max. 10 nm). In other words, this analysis is equivalent to seeing the plasma modified layer (ppMAH) as a strictly 2-D structure, regardless of thickness. The average surface chemistry from XPS measurements for all plasma treatments yielded an oxygen content of 31±2% (O 1s) and a carbon content of 69±2% (C1s).

Consistent results were found from the toluidine blue staining method, where the maximum number of carboxylic acid groups after full hydrolysis in the plasma layers was found to be the same within uncertainty, approx. 36 nmol/cm^2 (see Figure 1), i.e. it did not seem to be influenced by the plasma power level. We thus concluded that the changes of surface chemistry as a function of plasma power were negligible.

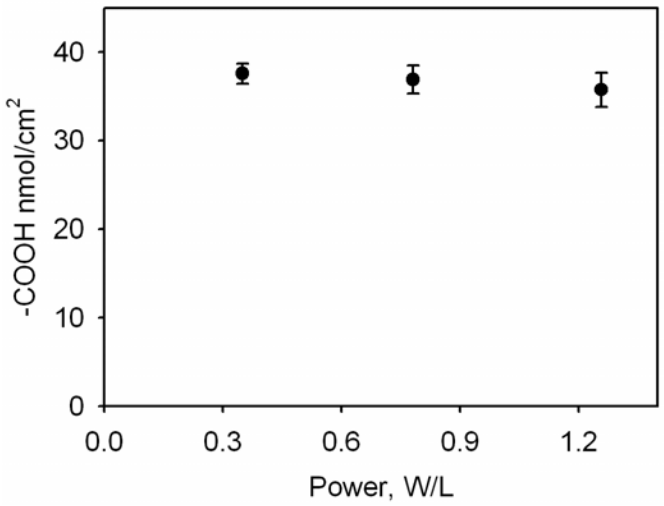


Fig. 1. Maximum number of carboxylic acid groups from toluidine blue staining method in the 80 nm thick films created with different power levels.

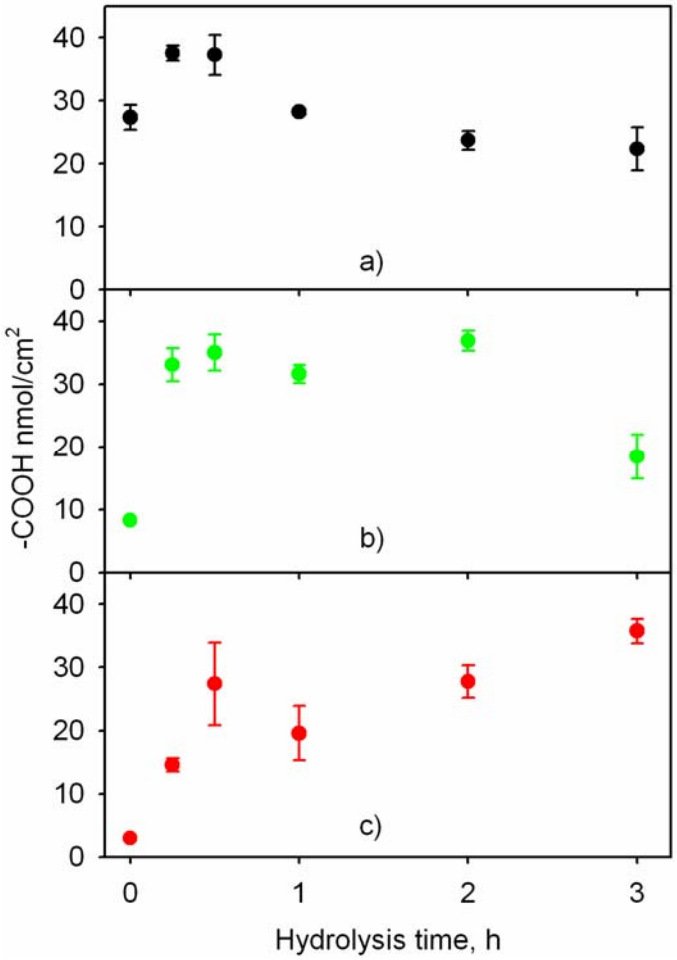


Fig. 2. Hydrolysis of preserved anhydride groups in a 80 nm plasma film created with different power levels as function of hydrolysis time in 0.1 mM NaOH: a) 0.3 W/l, b) 0.7 W/l 10 min, and c) 1.2 W/l, 8 min.

As mentioned above, in order to investigate the hydrolysis, films were placed into a 0.1 mM NaOH hydrolysing medium. As shown in Figure 2, the time evolution of the hydrolysis of the plasma polymerised layers of maleic anhydride is found to be strongly dependent on the plasma power used. The hydrolysis of ppMAH prepared with low power (Figure 2(a)) shows a tendency of fast hydrolysis and slow constant dissolution, i.e. a fast initial increase of the number of carboxylic acid groups, followed by a gradual decrease after a short time in sodium hydroxide. A similar trend was observed for the ppMAH prepared with medium power (Figure 2(b)). The hydrolysis of ppMAH made with high power (Figure 2(c)) progressed slower with a gradual increase in the number of carboxylic acid groups on the surface over time.

The observed slow increase in the number of carboxylic acid groups could be attributed to the cross-linking of the layers. The bonds prevent the swelling of the ppMAH layers (Chu et al (2006)), making it more difficult to hydrolyse the anhydride groups to carboxylic acid groups (Drews et al. (2007)). Similarly, the observed dissolution of the film could be an insufficient amount of cross-linking in the film and a high content of oligomers. An alternative explanation could be that the bonds are not between C-C (covalent bonds), as we would expect, but between C-O which during NaOH treatment can be hydrolysed.

The effect of plasma power can also be seen in the mechanical tests of the planar glassy carbon/epoxy specimens where ppMAH layers had been prior deposited on the glassy carbon surfaces. The substrates were plasma prepared with different plasma power levels from 0.3 W/l to 1.2 W/l. Figure 3 shows the dependence of interface fracture energy on the plasma power. The results show that there is an optimum plasma power value, 0.7 W/l, at which a very strong interface is obtained.

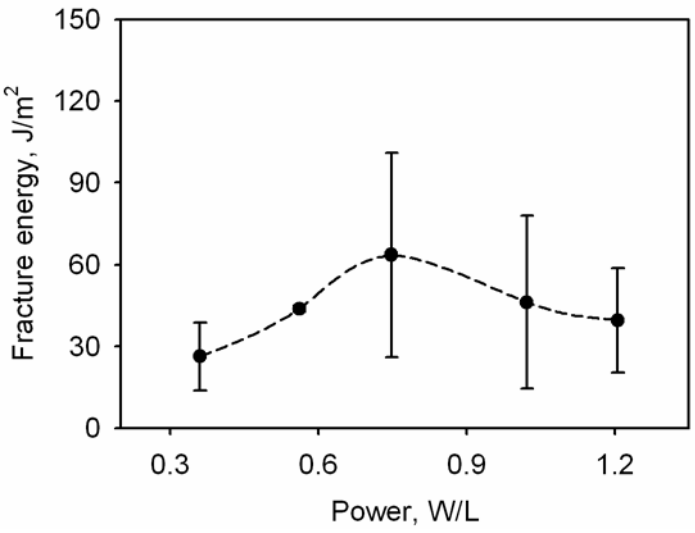


Fig 3. Fracture energy for crack initiation as a function of power level during ppMAH polymerisation (the polymerisation time is the same for all cases and equal to 10 min).

In Figure 4 the fracture resistance curves are shown for three different plasma treatments. For plasma power of 0.7 W/l the behaviour is significantly different from the other two treatments. Specimens prepared with a plasma power of 0.7 W/l exhibit a strong R-curve behaviour (increase of fracture energy with crack extension) and at some point unstable crack growth occurs. For the specimen shown in Figure 4 unstable fracture occurs after the crack has grown approximately 5 mm. On the other hand, specimens prepared with a plasma power of 0.3 W/l and 1.2 W/l show similar and stable crack growth up to approximately 10 and 15 mm,

respectively. The former could be evidence an extrinsic toughening mechanism (i.e. plasticity), whereas the latter would be a sign of low cohesion.

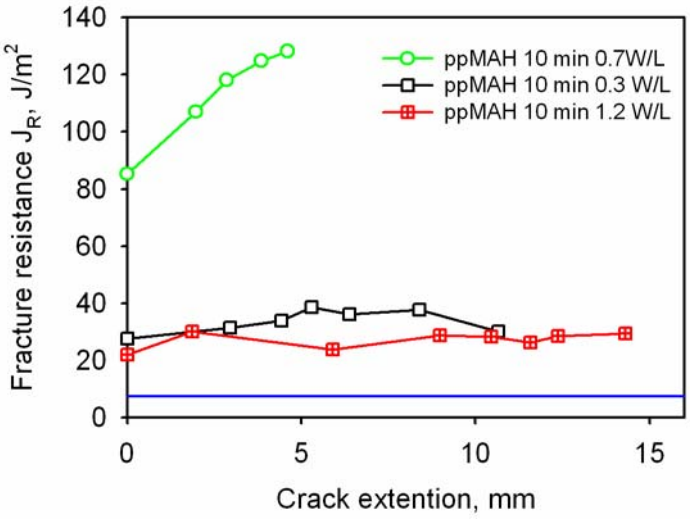


Fig. 4. Examples of fracture resistance curves of glassy carbon specimens prepared with different powers levels of ppMAH. The blue curve represents the value of untreated glassy carbon specimens (5-7 J/m^2).

Arguably the reason for the different behavior of glassy carbon treated at different plasma levels could be the different amounts of cross-links in the plasma layers. If the plasma layers contain many oligomers, i.e. if they are weakly cross-linked – Figure 5(c), the material would be expected to show low cohesion. On the other hand, materials which exhibit a high amount of cross-links (Figure 5(a)) would also be expected to show low cohesion, since the linear polymers between cross-links are short. According to the theory of elasticity of rubber based on thermal motions of ideal chains, cross-linked material can be only fully stretched up to $\sqrt{N}$ times, where N is the number of monomers (Doi, (1996)).

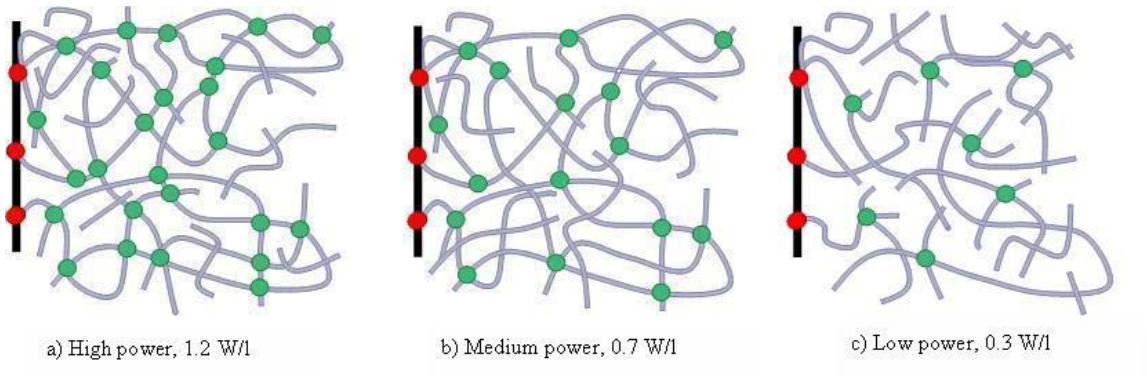


Fig. 5. Schematic illustration of the plasma deposited ppMAH layers. a) highly cross-linked layer, b) intermediate cross-linked layer and c) weakly cross-linked layer.

4. CONCLUSIONS

Using AC 2-phase plasma polymerisation technique it is possible to create a thin layer of maleic anhydride on glassy carbon and polyethylene substrates. If one considers these thin films only as

surfaces, the surface chemistry is not influence by the plasma power. This is confirmed by the toluidine blue staining method and XPS results. If we consider, however, these films as bulk materials we can see that there is a significant dependence on plasma level. This was shown in the case of hydrolysis of the layer with the toluidine blue staining method and through the mechanical tests (interface fracture under nominal Mode I). The experiments show that it is important to carefully optimise the conditions of creating the plasma layers. On one side, we can obtain a layer with strong adhesion between substrate and coating and a strong R-curve behaviour. On the other side, we can obtain a higly cross-linked layer. In this case the adhesion is weak and quite probably problems of self cracking due to internal stresses are introduced (Yu and Yasuda, (1999)). Finally it was shown (Figure 3) that it is possible, through the plasma polymerisation technique used, to obtain interfaces with unique properties. Weak, intermediate or strong interfaces could be easily manufactured giving the ability to design composites materials for specific applications.

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